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SPECIFICS OF DRYING OF BUILDING CERAMICS MADE USING LUBRICANT-COOLANT WASTE

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Based on a study of the main physicochemical processes in the clay – water – surfactant system, the paper shows the possibility of using coolant-lubricant liquids in the production of building ceramics without significant changes in the technological process. In this way the duration of drying is reduced, heat energy is saved, and the amount of waste is decreased.

Studying the effect of chemical reactants on the process of drying of ceramics is of interest for intensification of the process and establishment of a relationship between the physicochemical processes taking place in the clay – water – surfactant system and the drying regularities [1].

With account for environmental problems in utilization of machining-industry waste, water-emulsion wastes of lubricant-coolant liquids (Ukrinol-1, Akvol-10M, ÉT-2, Karbamol-P-1) were used as chemical reactants. The presence of anion-active and non-ionogenic surfactants in spent coolant-lubricant liquids (CLL) turns them into reactants with an overal improving effect that regulate the structural-rheological, moisture-conducting, and thermophysical properties of ceramic mixtures in the stages of molding and drying [2].

Mass exchange in the course of drying of colloidal capillary-porous bodies is determined by the set of physicochemical processes in the system, namely, osmotic diffusive moisture transfer, capillary liquid filtration, and effusive vapor transfer. According to the differential equation of the rate of drying [3]:

$$\frac{dP}{d\tau} = \frac{\lambda}{\rho_0 r^2 Q} \frac{(t_m - t_\tau)}{(1/3\varepsilon_{ph} - 1/\mathrm{Bi})},$$

where $dP/d\tau$ is the change in the material mass content per time unit; λ is the thermal conductivity; ρ_0 is the ceramic-material density; r is the sample radius; Q is the specific heat of the phase transformation; t_m is the temperature of the medium; t_τ is the material temperature (average); ε_{ph} is the phase-transformation criterion; Bi is the Biot number. The rate of change of the mass content is determined by the intensity of the phase transformations that occur in the system under the effect of the temperature gradient arising in the course of drying.

On the other hand, the moisture conductivity of a system depends on its thermodynamic state. The introduction of chemical reactants into a ceramic mixture helps to decrease the surface tension at the solid – liquid interface, which leads to an increase in the chemical potential $\Delta\mu_l$ of the system in accordance with the equation [4]

$$\Delta\mu_l = \mu_{l\,\infty} \frac{2\sigma}{r_c \rho_l},$$

where $\mu_{l\,\infty}$ is the chemical potential of the free liquid without taking into account the interphase reactions; σ is the surface tension; r_c is the average radius of the capillaries; ρ_l is the density of the liquid.

A decrease in the surface tension at the phase boundary decreases the capillary pressure, which is one of the driving forces of moisture transfer in drying. At the same time, the role of colloidal-chemical reactions affecting the diffusive process of moisture transfer is intensified.

The industrial wastes considered contain synthetic and semisynthetic coolant-lubricant components: oxyethylated alcohols, alkyl monosulfates, and sodium metasilicates, several synthetic-detergent ingredients, and emulsified oils, which increase the lubricating capacity of CLL with respect to the cutting tool [5].

The drying kinetics was studied on spondyl clay samples modified with water-emulsion CLL waste over a wide concentration range of the chemical reactants using a rapid thermogravimetric method for studying the drying properties of building ceramics [6].

The phase-transformation criterion was calculated using the Biot number [7]

$$\mathrm{Bi} = \alpha r/\lambda,$$

where α is the external heat exchange coefficient, W/(m^2 · K); r is the sample radius, m; λ is the thermal conductivity, W/(m · K).

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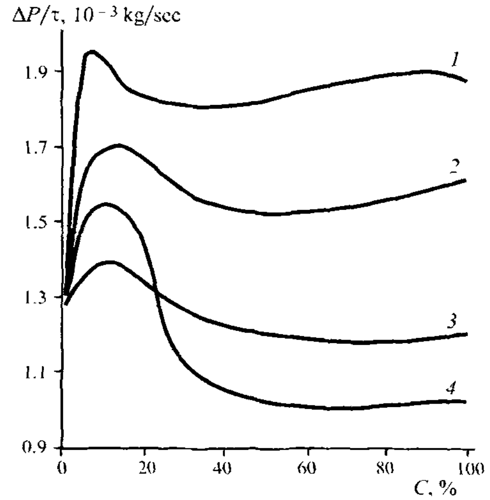

Fig. 1. Drying rate $\Delta P/\tau$ versus mass content C of spent CLL: *1*, *2*, *3*, and *4*) reactants Ukrinol-1, Akvol-10M, ÉT-2, and Karbamol-P-1, respectively.

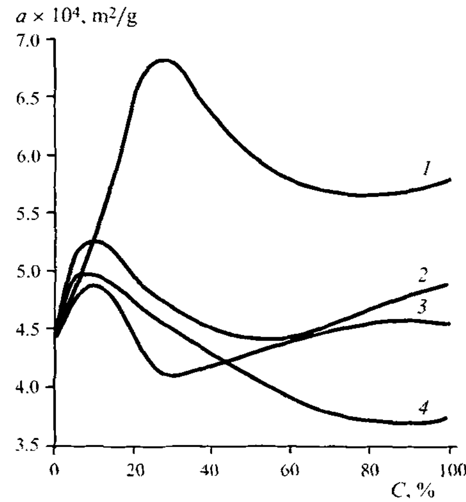

Fig. 2. Change in the internal mass transfer coefficient a versus mass content C of water-emulsion waste of CLL. Designations as in Fig. 1.

The coefficients α and λ were determined using methods of thermodynamic and thermogravimetric analysis [8]. The change in the energy of the bond between the moisture and the material under the effect of treatment with the CCL wastes was studied using the methods of adiabatic calorimetry and quantitative thermography [9, 10].

The study of the kinetics of ceramic-mixture drying in the presence of water-emulsion wastes of CLL made it possible to evaluate the effect of the reactants on the internal mass transfer. Figure 1 shows the functional relationships $dP/d\tau = f(C)$, where P is the mass content of the bonded material; kg; $dP/d\tau$ is the drying rate, kg/h; C is the mass content of the reactants, %.

As can be seen, additives of spent CLL foster the intensification of the drying process in accordance with their chemical composition and concentration. With the content of introduced additives equal to 10 – 25%, the internal mass transfer coefficient increases (Fig. 2), which is the evidence of intensification of the drying process. Thus, in using Ukrinol-1 and Akvol-10M, the drying rate increased 1.4 – 1.6-fold. In the indicated concentration range, adsorption of organic molecules on the solid surface results in its partial hydrophobization, the extent of which is determined by the chemical nature of the surfactants comprising the CLL. This is substantiated by the change in the heat of wetting of spondyl clay samples modified with the reactants considered (Table 1). A decrease in the energy of the bond of the moisture with the material is accompanied by a redistribution of the forms of bound moisture (Fig. 3). At the same time, the reactants ÉT-2 and Karbamol-P-1 in the indicated concentration range (10 – 25%) intensify drying to a significantly lesser extent, which is presumably due to the fact that the CLL contains non-ionogenic surfactants of the polyelectrolyte type, which bind substantial quantities of moisture (Table 1).

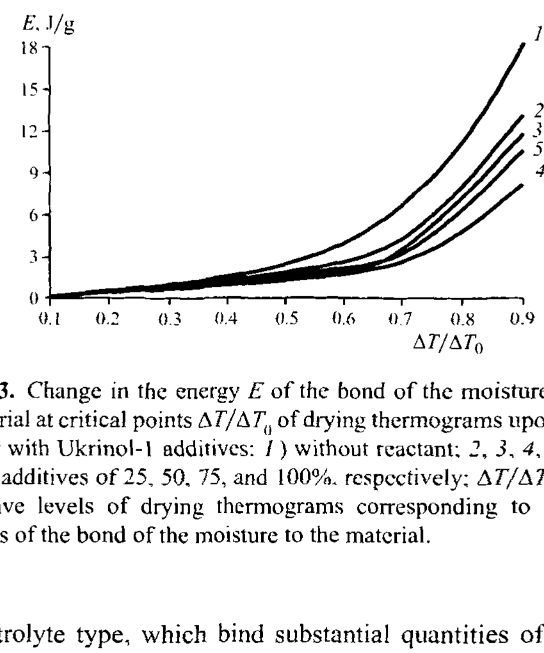

Fig. 3. Change in the energy E of the bond of the moisture to the material at critical points $\Delta T/\Delta T_0$ of drying thermograms upon treatment with Ukrinol-1 additives: *1*) without reactant; *2*, *3*, *4*, and *5*) with additives of 25, 50, 75, and 100%, respectively; $\Delta T/\Delta T_0$ is the relative levels of drying thermograms corresponding to various forms of the bond of the moisture to the material.

With a reactant content of 10 – 25%, internal moisture transfer occurs mainly by capillary liquid filtration and effu-

TABLE 1

Reactant	Heat of wetting, 10^3 J/kg, of ceramic samples with the volume content of the reactant, %*				
	10	25	50	75	100
Ukrinol-1	4.17	13.43	12.14	10.88	11.85
Akvol-10M	17.32	16.28	21.54	22.79	22.48
ÉT-2	18.83	17.08	21.41	29.15	23.12
Karbamol-P-1	22.14	19.06	21.68	23.06	22.37

* The heat of wetting without adding a reactant is 19.92×10^3 J/kg.

TABLE 2

Reactant content,* %	Phase-transformation criterion on introducing spent CLL			
	Ukrinol-1	Akvol-10M	ÉT-2	Karbamol-P-1
10	0.78	0.92	0.88	0.62
50	0.44	0.12	0.26	0.18
100	0.42	0.18	0.20	0.22

* The phase-transformation criterion without adding a reactant is 0.298.

sive vapor transfer, with prevalence of the latter. This is substantiated by the calculated values of the phase-transformation criterion (Table 2) obtained using experimental data from studying the drying kinetics.

The intense mass transfer caused by a decrease in the energy of the bond of the moisture to the material and by moisture removal in drying fosters the appearance of a volume-stressed state in the ceramic mixture under the effect of the gradient of excess pressure. This results in experimentally confirmed disturbances in the body continuity, which precludes recommending the indicated reactant concentrations, unless the drying duration is extended.

Figure 4 presents the relationship between the surface tension of aqueous solutions of spent CLL and their content. Within the range of the critical micelle concentration (CMC) equal to 50 – 75%, associative interactions between the reactant molecules foster an increased role of the colloidal-chemical components of the mass-transfer process. Here, moisture transfer in the form of effusive vapor transfer and capillary liquid filtration decreases.

Association of reactant molecules in the volume of the liquid dispersion medium and in the surface adsorption layers results in formation of micelles with polar functional groups that actively react with the liquid phase. This fosters an increased quantity of osmotic (entropic) moisture and increased hydrophilicity of the surface, which is accompanied by a relative decrease in the coefficient of internal moisture diffusion.

In connection with this, moisture transfer in the range of the critical micelle concentration occurs mostly by diffusive osmotic moisture transfer. This is indicated by the change in the potential of the internal mass transfer and the phase-transformation criterion in using all types of considered reactants.

It is found that in the range of the critical micelle concentration, i.e., with an additive content of 50 – 75%, the drying duration decreased on the average by 15 – 20%, which resulted in savings of around 1 MJ of heat per 1000 conventional bricks. At the same time, the amount of brick waste in drying the intermediate product decreased by 2 – 3% as a consequence of the plastifying effect of the gelatinous ad-

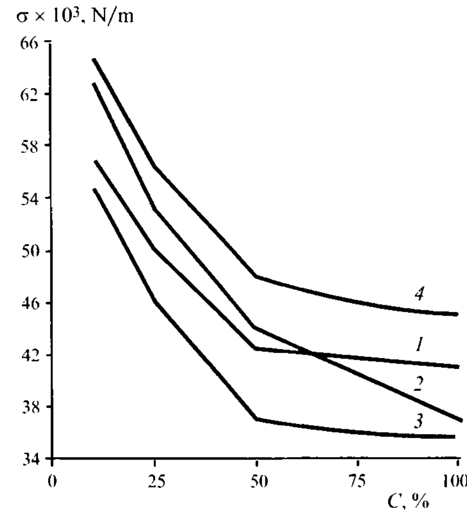

Fig. 4. Surface tension σ of water solutions of spent CLL versus mass content *C* of additives: *1*, *2*, *3*, and *4*) reactants Ukrinol-1, Akvol-10M, ÉT-2, and Karbamol-P-1, respectively.

sorption layers of the surfactant, which diminish the volume-stressed state of the material under the effect of temperature and moisture gradients and prevent disturbance of the sample integrity. The production technology using water-emulsion wastes of coolant-lubricants does not change substantially in this case.

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